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(54) Fuel additives and compositions

(57) Use, in order to improve the lubricity of low sulphur content fuel, of an additive comprising
A) a carboxylic acid amide,

and further comprising

B) a cold flow improver, and/or
C) an ashless dispersant.

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83% by weight dimer and 15% by weight of trimer and possibly higher acids. This "dimerized" acid, as well as the other acids described above, are commercially available or may be prepared by the application or adaption of known techniques.

The amide may be formed by reaction of the carboxylic acid with ammonia or a nitrogen-containing compound of formula (I):

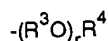


in which:

R¹ is an alkylene group containing from 2 to 10 carbon atoms;

q is 0 to 10;

Y is optionally N-substituted 1-piperazinyl where the substituent is a group R² or a group [R¹N(R²)]_qR² in which R¹ and q are as defined above, -N(R²)₂ or 4-morpholinyl; and each substituent R² is independently selected from hydrogen, alkyl having 1 to 6 carbon atoms and a group of formula:



in which:

r is 0 to 15;

R³ is an alkylene group having 2 to 6 carbon atoms; and

R⁴ is an hydroxyalkyl group having 2 to 6 carbon atoms, provided that at least one group R² is hydrogen.

When the compound of formula (I) contains more than one group R¹ the groups may be the same or different. The same is true when the compound contains more than one group R², more than one group R³ and more than one group R⁴.

The symbol q is preferably 0 to 5. The symbol r is preferably 0 to 10. R¹ contains preferably 2 or 3 carbon atoms. When R² is alkyl the moiety preferably contains from 2 to 4 carbon atoms. R³ is preferably an alkylene group having 2 to 4 carbon atoms. R⁴ is preferably an hydroxyalkyl group having 2 to 4 carbon atoms. The hydroxyalkyl group preferably contains 1 to 4 hydroxyl groups. When r is greater than zero R⁴ is preferably a mono-hydroxyalkyl group, for example hydroxyethyl or hydroxypropyl. When r is zero R⁴ is preferably a mono- or poly-hydroxyalkyl group having up to 4 hydroxyl groups, for example hydroxyethyl, hydroxypropyl or a 1-hydroxy-2,2-bis(hydroxymethyl)ethyl group. The number of carbon atoms in R¹ and the value q takes are selected independently. This means for example that when q is greater than zero, R¹ may be different in each repeat unit. Similarly, the number of carbon atoms in R³ and the value r takes are independent. This means that, for example, when r is greater than zero, R³ may be the same or different in each ether repeat unit.

According to a preferred embodiment, in the nitrogen-containing compound of formula (I) Y is -N(R²)₂, R² is ethylene and q is 0 to 3. Examples of such compounds include ethanolamine, diethanolamine, tris(hydroxymethyl)aminomethane, triethylene tetramine or diethylene triamine optionally N-substituted by two hydroxypropyl groups.

In another embodiment, in the nitrogen-containing compound Y of formula (I) is 4-morpholinyl or optionally N-substituted 1-piperazinyl, R¹ is an alkylene group containing 2 to 6 carbon atoms, q is 0 or 1 and each R² is hydrogen. Examples of such compounds include aminoethylpiperazine, bis-(aminoethyl)piperazine and morpholine.

The nitrogen-containing compounds of formula (I) are commercially available or may be made by the application or adaptation of known techniques. For example, the compounds of formula (I) in which r is 1 or more, i.e. those containing an ether or polyether linkage, can be prepared by reaction of a suitable amine, morpholine or piperazine compound with a molar excess of one or more alkylene oxides. When only one kind of alkylene oxide is used R³ and R⁴ contain the same alkylene moiety. When different kinds of alkylene oxides are used R³ and R⁴ may contain the same or different alkylene groups.

According to an embodiment of the invention, the amide A) contains at least one free carboxylic group in the acid-derived moiety. This kind of compound may be formed using a polycarboxylic acid as the starting acid, for example a dicarboxylic acid or a dimer or trimer acid. Suitably, the number of moles of reactants is controlled such that the resulting amide contains at least one free carboxylic functional group in the acid derived-moiety. For example, if an acid having two carboxyl functions is used, such as a dicarboxylic or dimer acid, the mole ratio could be about 1:1.

In the case that the amide contains at least one free carboxylic group in the acid-derived moiety, it may be used as is or it may be derivatised further to enhance its properties. The kind of compound used in further derivatising the

isobutylene or disobutylene.

The copolymers may be made by direct polymerization of comonomers, by transesterification, or by hydrolysis and re-esterification, of an ethylene unsaturated ester copolymer to give a different ethylene unsaturated ester copolymer.

5 Comb polymers are polymers in which branches containing hydrocarbonyl groups are pendant from a polymer backbone (see "Comb-Like Polymers. Structure and Properties", N.A. Plate *et al.* Poly. Sci. Macromolecular Revs., 8, pages 117 to 253 (1974)).

The hydrocarbonyl groups normally having from 10 to 30 carbon atoms and are bonded directly or indirectly to the polymer backbone. Examples of indirect bonding include bonding via interposed atoms or groups. This can include
10 covalent and/or electrovalent bonding such as in a salt.

The comb polymer is typically a homopolymer or a copolymer having at least 20 and preferably at least 40, and more preferably still at least 50, mole per cent of units having side branches containing at least 6, preferably at least 10, carbon atoms. It is possible for the comb polymer to contain units derived from other monomers.

15 Examples of comb polymers which may be used include homopolymers of, for example fumaric or itaconic acid, and copolymers of maleic anhydride, fumaric acid or itaconic acid with another ethylenically unsaturated monomer, such as an α -olefin, for example 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene and 1-octadecene or an unsaturated ester, for example, vinyl acetate. The copolymer may be esterified by reaction with an alcohol such as n-decan-1-ol, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, n-octadecan-1-ol, 1-methylpentadecan-1-ol or 2-methyltridecan-1-ol. Mixtures of alcohols may be used although it is preferred to use pure alcohols rather than the
20 commercially available alcohol mixtures.

Preferred comb polymers are the fumarate and itaconate polymers and copolymers for example as described in EP-A-153176, EP-A-153177, EP-A-225688, WO 91/16407, WO 95/03377 and WO 95/33805.

The preferred fumarate comb polymers are copolymers of (C_{12-20} alkyl) fumarates with vinyl acetate, especially those in which the alkyl groups have 14 carbon atoms or in which the alkyl groups are a mixture of C_{14}/C_{16} alkyl groups.

25 These may be made by known techniques.

Other suitable comb polymers which may be used include the polymers and copolymers of α -olefins and esterified copolymers of styrene and maleic anhydride and esterified copolymers of styrene and fumaric acid.

The comb polymers useful in the invention generally have a number average molecular weight, as measured by vapour phase osmometry, of 1,000 to 100,000, more especially 1,000 to 30,000.

30 Polar nitrogen compounds which may be used as cold flow improvers are known in the art and usually contain one or more of the same or different nitrogen-bound hydrocarbonyl groups, possibly in the form of a cation.

The hydrocarbonyl groups generally contain up to 40 carbon atoms. Examples of hydrocarbonyl groups include aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups typically contain 12 to 24 carbon atoms and are advantageously saturated.

35 The hydrocarbonyl groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group, such as keto, halo, hydroxy, nitro, cyano, alkoxy and acyl groups. If the hydrocarbonyl group is substituted, a single (mono) substituent is preferred. Examples of substituted hydrocarbonyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl and propoxypropyl.

40 The hydrocarbonyl groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include nitrogen, sulphur, and, preferably, oxygen. The hydrocarbonyl group may be bound to one or more nitrogen atoms via an intermediate linking group such as $-CO-$, $CO_2(-)$, $-SO_3(-)$ or hydrocarbonylene. When the polar nitrogen compound carries more than one nitrogen-bound substituent, the linking groups for each substituent may be the same or different.

45 The polar nitrogen compounds may contain amino substituents such as long chain $C_{12}-C_{40}$, preferably $C_{12}-C_{24}$, alkyl primary, secondary, tertiary or quaternary amino substituents. Preferably, the amino substituent is a dialkylamino substituent which may be in the form of an amine salt thereof (tertiary and quaternary amines can form only amine salts). The alkyl groups may be the same or different.

50 Examples of primary amino substituents include dodecylamino, tetradecylamino, cocoamino and hydrogenated tallow amino. Examples of secondary amino substituents include dioctadecylamino and methylbehenylamino. Mixtures of amino substituents may be present such as those derived from naturally occurring amines. A preferred amino substituent is the secondary hydrogenated tallow amino substituent, the alkyl groups of which are derived from hydrogenated tallow fat. These are typically composed of approximately 4% C_{14} , 31% C_{16} and 59% C_{18} n-alkyl groups by weight.

55 The polar nitrogen compounds may contain imino substituents such as long chain $C_{12}-C_{40}$, preferably $C_{12}-C_{24}$, alkyl substituents. The substituents may be monomeric (cyclic or non-cyclic) or polymeric. When non-cyclic, the substituent may be obtained from a cyclic precursor such as an anhydride. The cyclic precursor may include homocyclic, heterocyclic or fused polycyclic assemblies, or a system where two or more identical or different such cyclic assemblies are joined to one another. Where there are two or more such cyclic assemblies, the substituents may be on the same

polyoxyalkylene glycol group of number average molecular weight (by GPC) up to 5,000, preferably 200 to 5,000 (see EP-A-61895 and in USP 4,491,455).

Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are also suitable as the cold flow improver B). Here mention may be made to the stearic or behenic diesters of polyethylene glycol, polypropylene glycol or polyethylene/polypropylene glycol mixtures are preferred.

Examples of other linear cold flow improver compounds are described in Japanese Patent Publications Nos. 2-51477 and 3-34790, EP-A-117,108, EP-A-326,356, WO 95/03377 and WO 95/33805. Cyclic esterified ethoxylates are described in EP-A-356,256.

As noted above, mixtures of these cold flow improvers may be used, for example mixtures of ethylene-unsaturated ester copolymers and comb polymers, for example a mixture of an ethylene-vinyl acetate copolymer and a fumarate comb polymer.

Component C)

Ashless dispersants which may be used in the invention as component C) are well-known in the art. Examples include carboxylic ashless dispersants, for example polyamine succinamides and polyamine succinimides, Mannich base dispersants (comprising the reaction product of an alkyl phenol with an aliphatic aldehyde and a polyamine), and polymeric polyamine and hydrocarbyl polyamine dispersants. These kinds of dispersant are described in greater detail in for example EP-A-0531000. The use of polyamine succinimide and Mannich base dispersants is preferred.

Succinimide dispersants may be prepared by reacting a substituted succinic acylating agent with an amine/alcohol or an amine alcohol mixture. The succinic acylating agent may be derived from a polyalkene, such as polyisobutene, having a number average molecular weight as measured by GPC of 500 to 8000, for example 900 to 2100, and more particularly 950 to 1300.

Examples of amines which may be used include polyamines containing at least one primary amino group and on average at least two other nitrogen atoms in the molecule. Mention may be made of diethylene triamine, triethylene tetramine, tetraethylene pentamine and pentaethylene hexamine, and mixtures thereof. The reaction ratio of succinic acylating agent to amine is commonly from 1:1 to 2.0:1, preferably between 1.3:1 to 1.8:1, for example about 1.6:1.

The invention further provides a low sulfur fuel comprising component A) and further comprising components B) and/or C). Such fuel is formulated by simple mixing of the base fuel and the additive constituents in the desired proportions. The base fuel may be a middle distillate fuel or a bio-diesel fuel as described above. Component A is usually present in the fuel in an amount up to 500 ppm, preferably from 15-350, and most preferably from 20-200, ppm. When used, component B is usually present in an amount up to 1000 ppm, preferably from 100 to 500, and most preferably from 200 to 400, ppm. When used, component C is usually present in an amount up to 400 ppm, preferably from 25 to 200, and most preferably from 50 to 150, ppm. These amounts are expressed on a volume for volume basis and thus represent concentrations in microlitres per litre of fuel.

For the sake of convenience, the additives of the invention may be provided in the form of a concentrate for dilution with fuel. Such a concentrate forms part of the present invention and typically comprises from 99 to 1% by weight additive and from 1 to 99% by weight of solvent or diluent for the additive which solvent or diluent is miscible and/or capable of dissolving in the fuel in which the concentrate is to be used. The solvent or diluent may, of course, be the low sulfur fuel itself. However, examples of other solvents or diluents include white spirit, kerosene, alcohols (e.g. 2-ethyl hexanol, isopropanol and isodecanol), high boiling point aromatic solvents (e.g. toluene and xylene) and cetane improvers (e.g. 2-ethyl hexylnitrate). Of course, these may be used alone or as mixtures.

The concentrate or fuel may also contain other fuel additives in the appropriate proportions thereby providing a multifunctional fuel additive package. Examples of conventional fuel additives which may be used include fuel stabilisers, detergents, antifoams, cetane number improvers, antioxidants, corrosion inhibitors, antistatic additives, biocides, dyes, smoke reducers, catalyst life enhancers and demulsifiers. The total treat rate for multifunctional formulations containing the lubricity enhancing additives described is typically 25 to 2000 ppm, more usually 60 to 1200 ppm.

The invention also provides a method of reducing fuel pump wear in an engine which operates on a low sulfur-content fuel by using the low sulfur-content fuel described herein. The fuel may be used to reduce wear in rotary and in-line fuel pumps, for example as found in diesel engines, or in fuel transfer pumps. The latter are positioned between the fuel tank and the high pressure fuel pump. The fuel is particularly well suited for reducing wear in fuel injector pumps. The fuel may also be used to reduce wear in the latest fuel injector units which combine fuel pump and injector mechanisms. The invention is particularly well-suited to the operation of diesel and jet engines.

The present invention is illustrated in the following example.

Example

The lubricity of a number of diesel fuels was assessed using the High Frequency Reciprocating Rig (HFRR) test

Component A is oleyl diethanolamide;

Component B, the cold flow improver, is a commercially available ethylene-vinyl acetate copolymer of a type commonly used in middle distillate fuels having a broad boiling range (20-90 vol% distilling within a band of 100-120°C), the final boiling temperature being between 360 and 380°C.

Component C, the ashless dispersant, is a polyisobutenyl succinimide derived from polyisobutene having a number average molecular weight of 950. The amine used in preparation of the succinimide was tetraethylene pentamine.

The results obtained clearly demonstrate the improvement in lubricity associated with fuels in accordance with the present invention. The base fuel, run 1, has a very low inherent lubricity resulting in a relatively large mean wear scar diameter in the HFRR test of 650 μm . Similarly poor results are observed in runs 2-5. In runs 2-4 the fuels tested contain only one of components A, B or C. In run 5 the fuel contains components B and C but no component A.

In contrast, runs 6-8, particularly run 8, show a significant improvement in lubricity expressed as a much smaller mean wear scar diameter. It should be noted in runs 6-8 the amounts of components A, B and C are the same as in earlier runs. The fact that much improved lubricity is observed clearly shows that there is a synergistic interaction between the components, i.e. between A and B in run 6, between A and C in run 7 and between A, B and C in run 8. It will be appreciated that this synergistic relationship could enable the amounts of components A, B and/or C to be reduced without significant detriment to the lubricity of the fuel to which the components are added. In turn this could allow savings in materials used.

The synergistic interaction between components A and B was confirmed in a number of other experimental runs as reported in Tables 2 to 6 below.

Table 2

Run No.	Component and amount (ppm v/v)		HFRR @ 60°C
	A	B	MWSD (μm)
9	0	200	645
10	25	200	525

Components A and B were the same as in Table 1 above.

Table 3

Run No.	Component and amount (ppm v/v)		HFRR @ 60°C
	A	B	MWSD (μm)
11	0	200	670
12	25	200	360

Component A was as above. Component B, the cold flow improver, was a commercially available ethylene-vinyl acetate copolymer of a type commonly used in middle distillate fuels having a broad boiling range (20-90 vol% distilling within a band of 100-120°C), the final boiling temperature being between 360 and 380°C.

Table 4

Run No.	Component and amount (ppm v/v)		HFRR @ 60°C
	A	B	MWSD (μm)
13	0	200	675
14	25	200	485

Component A was as above. Component B, the cold flow improver, was a commercially available modified ethylene-vinyl acetate copolymer of a type commonly used in middle distillate fuels having a narrow boiling range (20-90 vol% distilling within a band of 100°C or less), the final boiling temperature being about 360°C.

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9. A concentrate comprising from 99 to 1% by weight of an additive as defined in any one of claims 1 to 6 and from 1 to 99% by weight of solvent or diluent for the additive which solvent or diluent is miscible with and/or capable of dissolving the additive in a low sulphur content fuel.

5 10. A method of reducing fuel pump wear in an engine which operates on a low sulphur content fuel which method comprises using as the low sulphur content fuel the fuel claimed in claim 7 or 8.

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(54) **Fuel additives and compositions**

(57) Use, in order to improve the lubricity of low sulphur content fuel, of an additive comprising
A) a carboxylic acid amide,

and further comprising

B) a cold flow improver, and/or
C) an ashless dispersant.

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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 3360

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 5 338 470 A (HIEBERT ET AL.) * claim 1; tables 1,2 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 5 November 1997	Examiner De La Morinerie, B
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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